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## Effect of Graft Copolymer on Protection of Homopolymer from Precipitation

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Precipitation of polymethyl methacrylate (PMMA) from dimethyl sulfoxide solution by addition of water as a precipitant was studied in the presence of a well-characterized graft copolymer of polyvinyl alcohol (PVA). The graft copolymer prepared by a radiation method and freed from homoPMMA and homoPVA had one PMMA branch whose length was nearly equal to that of the PVA backbone.

Even when such an amount of water was added to PMMA solution as to cause all the PMMA to precipitate from the solution, the precipitation was prevented by the presence of relatively small amounts of the graft copolymer. With decreasing molecular weight of PMMA, the effect of protection became much more prominent. When the precipitation was prevented, the solution was transformed into a stable emulsion. The protection mechanism against precipitation was discussed on the basis of the results obtained and electron microscopic photographs of the emulsion particles.

### INTRODUCTION

Block and graft copolymers have sequences of different monomer units in a molecule. These copolymers are, therefore, expected to exhibit a number of unique properties which can not be observed when the corresponding homopolymers are employed. One of them may be an emulsifying power as observed with low molecular weight surfactants. For instance, Hughes and Brown<sup>1)</sup> found that solutions of polystyrene-polyethyl acrylate mixture prepared from polymerization product of styrene in polyethyl acrylate emulsion consisted apparently of a single, hazy phase, while the physical mixture of these homopolymers separated distinctly into two layers when dissolved in common solvents. A similar phenomenon was also reported by Molau in several polymer-polymer systems.<sup>2)</sup> He concluded that this should be due to emulsifying ability of the graft copolymer which might have been formed during polymerization, and accumulated on the surface of droplets of polymer solution.

Recently Wellons and co-workers<sup>3)</sup> found a particularly interesting property of graft copolymer; films cast from solutions of two immiscible homopolymers containing a small amount of the corresponding graft copolymer were transparent, while those prepared from mixture of homopolymers without copolymer were translucent. This effect of graft or block copolymers was studied more extensively by Riess and co-workers,<sup>4-6)</sup> and it was shown that the incompatibility of two homopolymers could be reduced by addition of block copolymer

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which acts as an emulsifier.

It is frequently pointed out<sup>7)</sup> that isolation of graft copolymers by means of fractional precipitation technique from a reaction mixture which contains usually two homopolymers corresponding to backbone and branch, is awfully tedious, since a stable colloidal suspension is readily formed which resists flocculation by most of the common methods. It seems highly plausible that this undesirable stabilization of colloidal solutions is just a consequence of the above mentioned emulsifying effect of the co-existing graft copolymer.

The purpose of this work is to investigate more or less quantitatively the emulsifying effects of graft copolymers using well-characterized samples. In the present paper we will report the effect of graft copolymer on the protection of the corresponding homopolymers against precipitation from the solution caused by addition of the precipitant. The graft copolymer used here is poly(vinyl alcohol-g-methyl methacrylate). It has one graft branch whose length is approximately equal to that of the backbone. The homopolymer to be protected from precipitation is polymethyl methacrylate(PMMA) with various degrees of polymerization. Dimethyl sulfoxide(DMSO) was used as a common solvent, and water as a selective precipitant of PMMA.

## EXPERIMENTAL

### Preparation and Characterization of the Graft Copolymer

The PVA-MMA graft copolymer was prepared by mutual irradiation grafting of MMA onto water-swollen PVA films in the presence of methanol and trichloroethylene. The latter was used as a chain transfer agent to make the branch length comparable to that of the backbone polymer. Isolation of the graft copolymer from the reaction mixture was effected by alternate extractions of homoPMMA and unreacted PVA with benzene and water-*n*-propanol (75-25) mixture at the boiling points. The extraction was repeated as long as extractable PVA or PMMA molecules were present in the residue. The polymer remaining after the complete extraction was regarded as a pure graft copolymer. The number-average molecular weights of the graft copolymer, backbone and graft branch were determined by osmotic pressure measurements in benzene, after complete acetylation of PVA part of each polymer. The branch was separated from the graft copolymer by oxidative cleavage of 1,2-glycols in the PVA backbone with periodic acid. From the molecular weights and the chemical composition of the graft copolymer the structure could be made clear as follows. The number of graft branch per each graft copolymer molecule was unity, and the degree of polymerization (DP) of the branch and the backbone were 1,810 and 2,140, respectively.

The more detailed grafting procedure and characterization method were described in a recent paper.<sup>8)</sup>

### Homopolymers

HomoPMMA's with DP of 1,040, 1,500 and 1,770 were those which were

formed in the interior of PVA films during grafting. HomoPMMA with DP of 3,540 was obtained by bulk polymerization using azo-bisisobutyronitrile as an initiator. The DP was measured osmotically in every case and all the samples were used without fractionation.

### Precipitation Equilibrium

The homoPMMA and the graft copolymer were dissolved at the same time in DMSO in test tubes, the concentration of homoPMMA being always maintained at 1 % and that of the graft copolymer being varied widely. A known amount of water was added to the solution at room temperature and the tube was sealed. The sealed tube was then heated on a boiling water bath to redissolve the polymers which had been precipitated by the addition of water. After complete dissolution, the tube was put in a thermostat at 30°C for 48 hrs to equilibrate the precipitation or the liquid-liquid phase-separation. The equilibrium was reached mostly within a day.

The polymer precipitated to equilibrium was isolated from the solution by decantation (in an exceptional case centrifugation was applied), washed with methanol or water, dried and weighed. In the case of phase-separation, the higher concentrated phase was separated from the less concentrated upper liquid phase by decantation and the polymer was recovered by addition of methanol or water.

## RESULTS

### Solubility of Pure Graft Copolymer

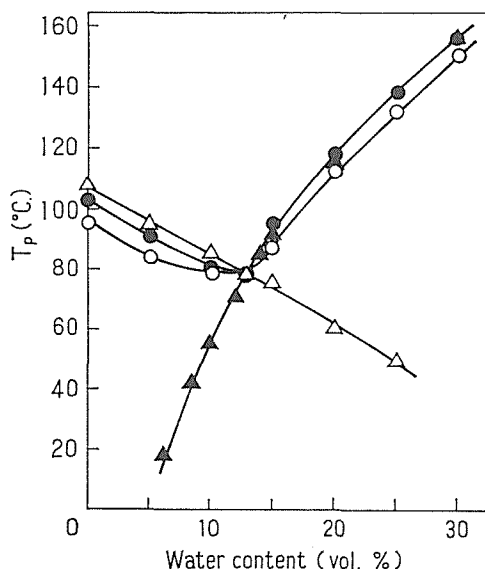


Fig. 1.  $T_p$  of various polymers in DMF-water mixtures (polymer conc.=1.0 wt%).  
 ○: PVA-MMA graft copolymer, ●: homoPVA-homoPMMA blend, △: homoPVA (DP=2,000), ▲: homoPMMA (DP=1,770).

In order to study the effects of addition of graft copolymer to solution of homopolymer, solution behaviors of pure graft copolymer should be known first of all. From this point of view the solubility of PVA-MMA graft copolymer was studied briefly in dimethyl formamide (DMF)-water mixtures. The result was shown in Fig. 1, together with those of the parent homopolymers. The mixed solvent was chosen, because it was convenient for the comparison of solubility differences between the graft copolymer and the homopolymers.

As can be seen from the figure, the incipient precipitation temperature  $T_p$  of the graft copolymer is governed expectedly by that of the component polymer which precipitates under the same mixture composition. The most noticeable feature seen in Fig. 1 is that  $T_p$  of the graft copolymer is always lower than that of the homopolymer blend except at a water content of 13 % where both homopolymers give the same  $T_p$ . Thus it is evident that there is a temperature range or a composition region of the solvent mixture where either of the homopolymers is precipitated, but the graft copolymer is still dissolved. A similar trend was also observed by several authors.<sup>9,10</sup> This delay of the onset of the precipitation, *i.e.*, the apparent increase in solubility of the graft copolymer may be due mainly to steric interference of the dissolved component polymer chains against aggregation of the other component polymers which, otherwise, would readily come to coagulation. This explanation is also supported by the fact shown in Fig. 1 that at a water content of 13 % where both homopolymers were precipitated at the same temperature the precipitation of the graft copolymer also occurred. It seems likely that the graft copolymer molecules aggregate to polymolecular micelles near the point of precipitation, as Dondos and co-workers<sup>11</sup> confirmed by means of light scattering study.

In the present work the emulsifying effect of the graft copolymer was studied under the condition that only one of the homopolymers is precipitated, while the graft copolymer is still held in the solution. The solvent-precipitant combination adopted here was not DMF-water but DMSO-water, since the required condition was fulfilled readily even at ordinary temperature in the latter case. The concentration of homoPMMA in DMSO was kept at 1 % and various amounts

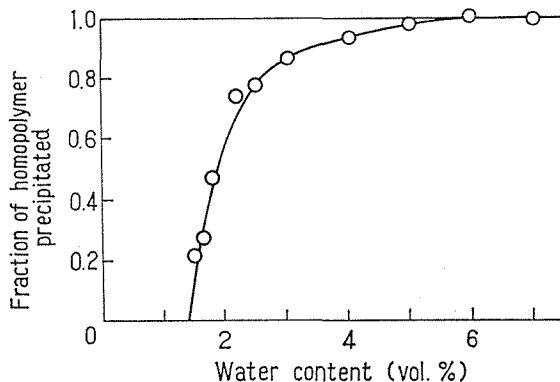


Fig. 2. A precipitation curve of homoPMMA in DMSO-water mixtures (initial polymer conc.=1.0 wt%, DP=1,500, temp.=30°C).

of the precipitant ( $\text{H}_2\text{O}$ ) were added.

Figure 2 shows the precipitation curve of homoPMMA in DMSO-water mixture at  $30^\circ\text{C}$ . As is seen, the amount of water required to cause precipitation of all the PMMA is very small. The graft copolymer was not precipitated at all by addition of such a small amount of water.

### Emulsification of Homopolymer by Graft Copolymer

Influence of the added graft copolymer on the incipient precipitation point of homoPMMA was shown in Fig. 3.

The presence of graft copolymer does not affect the precipitation points of the solution of homoPMMA, indicating that aggregation of homopolymer molecules was not interfered with the existing graft copolymer, at least, by such a small amount of graft copolymer.<sup>12)</sup> However, amounts of the homoPMMA precipitated in the bottom of tubes were decreased distinctly, when the graft copolymer was present in the solution. The appearance of the solution changed in the following fashion.

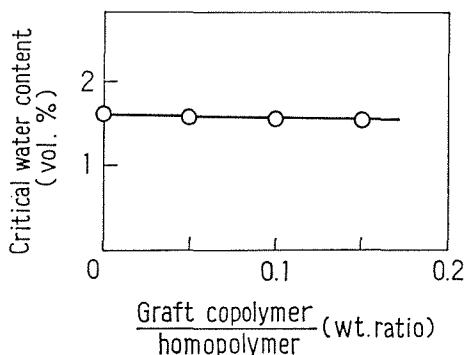


Fig. 3. Influence of PVA-MMA graft copolymer on the critical water content necessary for the incipient cloud point of homoPMMA in DMSO-water mixtures (conc. of homopolymer=1.0 wt%, DP=1,500).

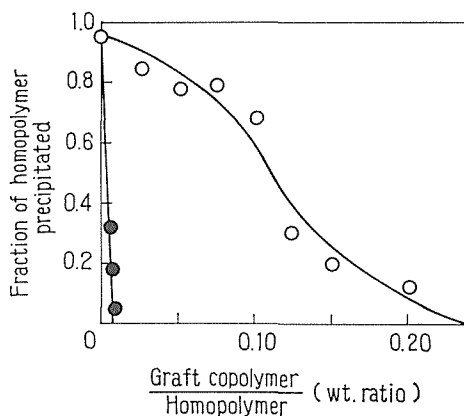


Fig. 4. An example of the protection effect of PVA-MMA graft copolymer on the precipitation of homoPMMA. The polymer precipitated was separated by simple decantation (●) or under centrifugation (○). (DP=1,040).

When the graft copolymer was absent, the DMSO solution of PMMA became hazy upon addition of water, and then separated into two clear layers within one day. In case that the amount of added water was sufficient enough, the upper phase contained practically no polymer, while the lower phase consisted of swollen, precipitated homoPMMA. This is quite the well-known phenomenon observed with ordinary solutions of homopolymers. However, when the graft copolymer was present in the solution, the appearance of the upper phase changed from clear to turbid and the amount of homopolymer precipitated in the bottom was decreased with increasing amount of the added graft copolymer and finally became zero.

A typical result is given in Fig. 4. The amount of water was adjusted so as to precipitate the homoPMMA just to completion when the graft copolymer was not added. It can be clearly seen that the precipitation of homoPMMA was greatly protected by the presence of the graft copolymer. In other words, one can say that the homopolymer was emulsified by the graft copolymer. The minimum amount of the graft copolymer to be added to cause the precipitated polymer phase to disappear was as small as 1 % of homoPMMA. In this case the solution became turbid on the whole and the turbid appearance was kept unchanged at least for six months. Even if the turbid solution was subjected to centrifugation of 24,200 g for 10 min., a considerable amount of homoPMMA was still held in dispersion without precipitation. The result was given also in Fig. 4.

DP of the homoPMMA used in the above experiment was 1,040. The following studies were carried out to see the effect of the DP of homoPMMA on its emulsification and the results were given in Fig. 5. The precipitated polymer was separated by decantation. As is obvious from Fig. 5, the emulsifying effect of graft copolymer for the homopolymer became more prominent as the DP of homoPMMA was lower. The similar large dependence of DP of homopolymer has been also reported by other workers in the study of compatibilization effects of block copolymer on immiscible homopolymers.<sup>4-6,13,14)</sup>

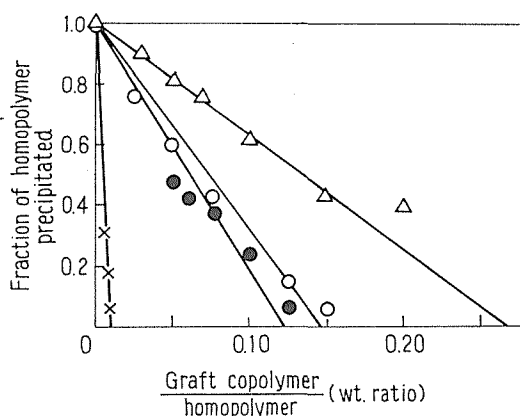


Fig. 5. The protection effect of PVA-MMA graft copolymer on the precipitation of homoPMMA with various DP's.

× : DP=1,040, water content=5.0 vol%  
 ● : " =1,500, " =6.0 "  
 ○ : " =1,770, " =4.0 "  
 △ : " =3,540, " =3.5 "

In the above experiments a critical amount of water was added which was required to just cause all homopolymers to be precipitated when the graft copolymer was absent. Figure 6 shows the results obtained at experiments whereby the water was added to a smaller extent than the critical amount. It is seen that a plateau region appeared in the precipitation curves in this case. The upper solution layer was always clear in this concentration range of the

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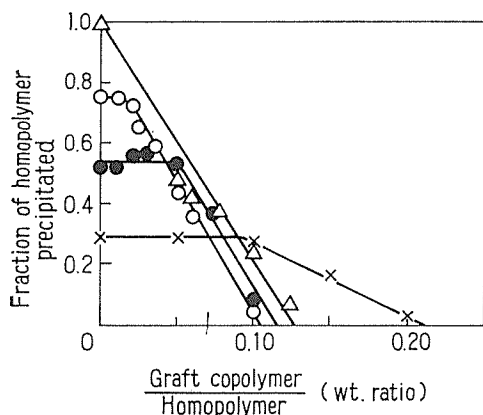


Fig. 6. Influence of the water content added by smaller amounts than to cause just total homopolymer to precipitate (DP=1,500).

x : water content=1.6 vol%  
 ● : " =1.8 "  
 ○ : " =2.3 "  
 △ : " =6.0 "

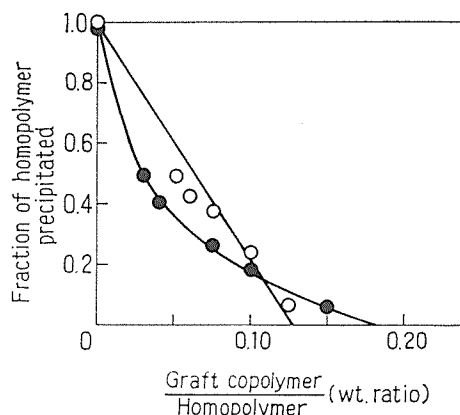


Fig. 7. Influence of the water content added by larger amounts than to cause just total homopolymer to precipitate (DP=1,500).

○ : water content=6.0 vol%  
 ● : " =8.0 "

graft copolymer, suggesting that the graft copolymer did not influence the phase-separation of homoPMMA solutions. However, when the amount of graft copolymer became higher than a certain threshold value, the emulsification took place, which led to a change in the appearance of the solution phase from clear to turbid.

On the contrary, the result given in Fig. 7 was obtained, when a larger amount of water was added than the critical amount. In this case, the precipitation of homopolymer could be prevented by a smaller amount of the graft copolymer, as far as the added amount was small.

## DISCUSSION

According to a preliminary experiment, the PVA-MMA graft copolymer was found to be able to emulsify also homoPVA in DMSO-benzene mixture, where benzene is a good solvent for PMMA, but a precipitant for PVA. In this case, even when the DMSO solution was poured into a large amount of benzene, the solution containing the emulsified PVA molecules seemed quite clear to the naked eye, but microscopically not homogeneous, because Tyndall phenomenon was observed distinctly. Therefore, it may be concluded that the emulsification by a graft copolymers is not a specific effect observed only for some limited systems, but rather a general phenomenon and can be ascribed to the chemical structure characteristic to graft copolymers. (HomoPVA exhibited no protection effect of homoPMMA from precipitation.) The fact that colloidal dispersions of the homoPMMA are stable at least for six months, indicates the protecting force of graft copolymers to be relatively strong. It should be pointed out here that there is consequently considerable doubt as to whether the fractional precipita-



tion is a really effective method to separate the graft copolymer from the reaction mixture.

In order to clarify the mechanism by which the graft copolymer emulsifies the homopolymer, the following information obtained at studies carried out varying the precipitant amount seems to be useful.

When water was added to a smaller extent than the critical amount necessary to precipitate all the homoPMMA, but only enough to cause phase separation, no influence of the graft copolymer was observed so long as the amount of the graft copolymer was small. On the other hand, the emulsification by the graft copolymer took place obviously, when just the critical amount of water was added, and this effect became more prominent with addition of excess water. This means that a considerable amount of the graft copolymer is needed to influence the liquid-liquid phase-separation, but that a very small amount of the graft copolymer is sufficient to protect the homopolymer from precipitation.

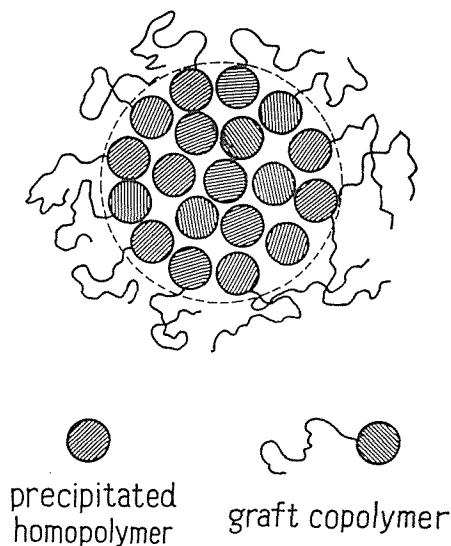


Fig. 8. Schematic representation of the protection mechanism.

By taking into consideration the above observations, the mechanism of emulsification of homopolymers by the graft copolymer may be proposed as illustrated schematically in Fig. 8. The homopolymer molecules aggregate with each other by the addition of the precipitant, resulting in formation of such large particles that cause the appearance of solution turbid. It seems very reasonable to believe that the PMMA part in the graft copolymer is also incorporated into the particle formation, whereas the other part cannot enter into the particle. Then it follows that the emulsion particles are surrounded by the PVA part of the graft copolymer which is in a dissolved state independent of the addition of the precipitant. As a result the particles may be held in dispersion by soluble PVA chains which form a peripheral outer shell, leading to prevention of particles from coagulation. It is interesting that this effect of graft copolymer is analogous to the emulsification of organic liquids in aqueous

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solutions of soap. As the driving force to aggregate PMMA molecules becomes stronger with increasing amount of added precipitant, the emulsifying effect of graft copolymer becomes more remarkable as shown in Fig. 7. However, the strong aggregation of PMMA molecules might lead, in turn, to a result that larger amounts of the graft copolymer than that is sufficient to just emulsify the homoPMMA are incorporated into the particles. Thus somewhat larger amounts of graft copolymer should be added in order to emulsify all the homopolymers.

Electron microscopic photographs shown in Fig. 9 also support the above mechanism of emulsification. The photograph of Fig. 9(a) was taken after a colloidal suspension containing 1 % homoPMMA and 0.15 % PVA-MMA graft

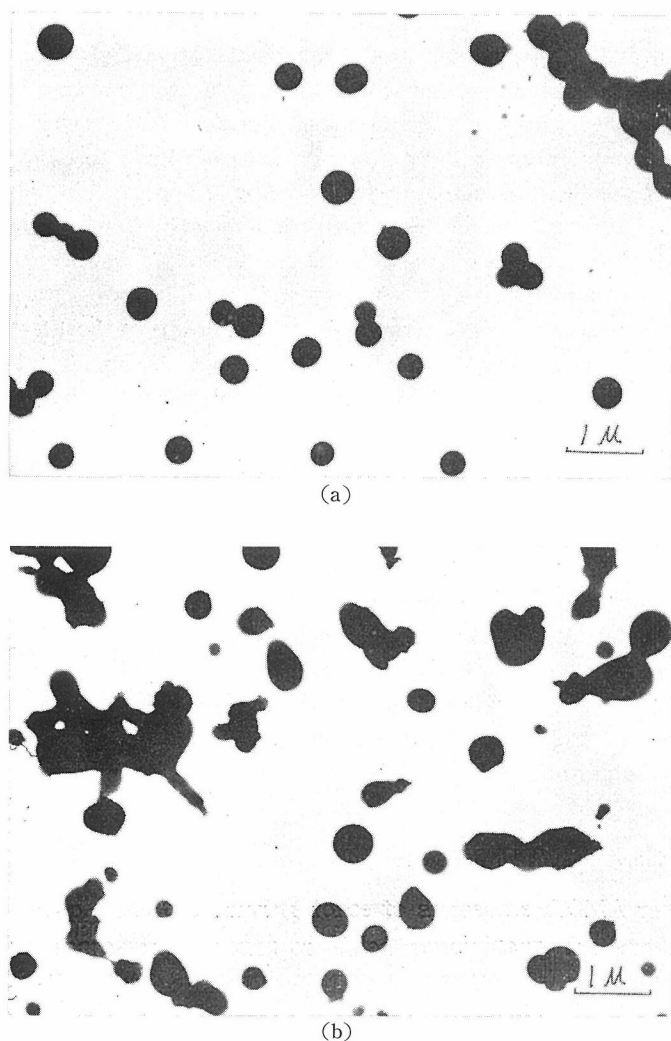


Fig. 9. Electron microscopic photographs of colloidal particles in the emulsion containing homoPMMA protected from precipitation by the presence of PVA-MMA graft copolymer. Concerning (a) and (b), see the text.

copolymer was dialyzed against water and condensed to dryness on a collodion film at room temperature. On the other hand, that of Fig. 9(b) was taken after the same suspension was coagulated by pouring into methanol, dried and then again dispersed on a collodion film. In both the photographs one can clearly see round particles which are similar to ordinary emulsion particles. It is interesting that spherical structure of the particles is apparently preserved in the solid state. According to the mechanism shown in Fig. 8, the shell of a spherical emulsion particle should consist of monomolecular layer of graft copolymer. We can test the validity of this assumption by calculation. The diameter of an emulsion particle was found to be  $0.35\mu$  from electron microphotographs of Fig. 9. The surface area of a particle is calculated to be  $38.5 \times 10^{-10} \text{ cm}^2$ , and the total surface area of the emulsion particle of 1 g homoPMMA to be  $144 \times 10^3 \text{ cm}^2$ . On the other hand, DP of a PMMA-branch of the graft copolymer is 1,810. If the branch has a spherical form, the diameter and cross sectional area of the sphere is calculated to be  $7.96 \times 10^{-7} \text{ cm}$  and  $49.8 \times 10^{-14} \text{ cm}^2$ , respectively. Since 0.15 g graft copolymer, therefore  $0.15 \times 0.66 \text{ g}$  branch of the graft copolymer has emulsified 1 g homoPMMA, we have to calculate the total cross sectional area of spheres of graft branch of 0.15 g graft copolymer. It was found to be  $163 \times 10^3 \text{ cm}^2$ . Agreement of this value with that of the total surface area of the emulsion particles is satisfactory. This is a definite support for the mechanism of the emulsification, that spherical emulsion particles have shells of monomolecular layer of graft copolymer. On this point more detailed investigations are currently being carried out. It is known also in the case of ordinary emulsions<sup>15)</sup> that a monolayer of emulsifier molecules covers the emulsion particles.

As is seen from Fig. 6, which shows the results obtained at the experiment of insufficient addition of water, the graft copolymer does not influence the phase-separation of homopolymer unless the amount is larger than a certain value. It is difficult at present to give a clear explanation for this. As is generally observed during the process to attain an equilibrium of liquid-liquid phase-separation, solutions become temporarily turbid upon addition of nonsolvent, and then separate gradually into two liquid layers. In the initial stage prior to the equilibrium establishment, most of the added graft copolymers may be regarded to be located in the interface of the unstable droplets present in the turbid solution, and thus to disturb the coalescence of each droplet which would lead otherwise finally to the phase-separation into two layers. If the density of the graft copolymer at the droplet surface is too sparse to prevent the droplet from coalescence, no effect of the graft copolymer might be expected. This mechanism is somewhat similar to that of Molau<sup>2)</sup> which was proposed to explain a polymeric oil-in-oil emulsion. It might be better to state simply that the solution concentration of graft copolymer should be higher than a critical value to emulsify the homopolymer, if one stresses the similarity of the present result with conventional emulsions where active surfactants are able to emulsify only when their concentration becomes higher than a so-called critical micelle concentration.

#### ACKNOWLEDGMENT

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